6031.2

1. Contractor's Name and Address:

Springborn Laboratories, Inc.
Department of Analytical Chemistry
Ten Springborn Center
Enfield, CT 06082

2. Title of Report:

Development of Acceptance Criteria for Batches of Silane Primer for External Tank Thermal Protection System Bonding Applications

December 1, 1984 - March 1, 1985

3. Date of Publication:

April 10, 1985

4. Type of Report and Contract Number:

9th Progress: NAS8-35818

5. Author(s):

F. Mikes

6. Prepared For:

C. Marshall Space Flight Center, AL 35812

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AT01 - 1x
EM13B-18/Blevins - 1x
EH33/Morris - 10x
NASA Scientific & Technical Info. Facility - 1x + Repro.

LIST OF CONTENTS

NOTE: In our 7-8 Report, please make a correction on page 9, 5th line from bottom: Samples 7""-6"", 13"", C"" - this should read: Samples 7'''-6''', 13''', C''', etc.

TABLE I*

DC 1200 Primer Lots Used in Project Program

Springborn Labs ID #	DC Primer Lot #	Date Received at Springborn	Additional Description and Further Sample Labeling
A**	QL033703	5/11/83	red opaque
B**	QL071621	11/29/83	red, leaked
C**	QL093752	11/29/83	clear, sealed
1***	EN057367	3/30/84	clear
2***	QL033705	3/30/84	red
3***	063711	3/30/84	red, S/L Exp 6/84, Temp 50/90F RS3.900324, 7/83 MMSK343A025 83G382
4***	093713	3/30/84	red, S/L Exp. 09/84, Temp 50/90F, RS3.794481 09/83 MMSK343A025 83G530 (hold for J Mills)
5***	093733	3/30/84	red, S/L Exp 09/84, Temp 50/90F, RS3.794481, 09/83 MMSK34A025 83G529
6***	071620	3/30/84	red, S/L Exp 7/82, Temp 50 to 90F, RS1:705481, 08/81 MMSK343A025 81G464
7+	QL103753	1/10/85	red

*A sample identification table is included as the first page in each report.

**Three (3) DC 1200 Primer Lots acquired by Springborn Laboratories for initial tests (see monthly reports 1, 2 and 3).

***Six (6) DC 1200 Primer Lots received from NASA, Management Division Bldg. 4471, on March 30, 1984.

+DC 1200 Primer Lot received from NASA, Bldg. 4612, Mr. Don Morris, Project Monitor.

2. TGA and FTIR Analysis of DC 1200 Silane Primers - Concluding Tests

In order to compare TGA thermograms of all submitted silanes, additional TGA profiles of samples #B and #C were obtained (Fig. 1). Sample #C was also reexamined -- its TGA profile is compared to the one obtained earlier (10/8/84) in Fig. 2. (FTIR analysis of this sample did not indicate any significant increase in OH-absorption since the last TGA analysis.)

A new DC 1200 primer sample was obtained from NASA-MSFC on 1/6/85 (our ID #7). Its TGA and FTIR profiles were recorded and are enclosed as Figs. 3 (FTIR) and 4 (TGA).

New FTIR spectra of samples B and C were also obtained as shown in Figs. 5 (B) and 7 (C). A visual comparison of the three IR spectra (samples B, C, 7) indicate that sample #7 (new silane lot) does not contain any OH-absorption and thus has not undergone any hydrolysis. On the other hand, substantial OH-absorption is observed in primer sample #B (more than in the last FTIR scanning on 7/11/84). The largest OH-absorption is in sample #C as expected (see previous 7-8th report, 12/7/84).

TGA profiles of all silane primers received from NASA-MSFC to date are graphically presented in Fig. 7. Samples exhibiting similar thermograms are indicated in the table below. This table replaces a similar one given in the 7-8th report on page 5.

Similarity Group	TGA* Profiles of DC 1200 Primer Lots #	See Fig. No.
I	1, 2, 3, 5, ---(4, 6)	7
II	7	4
III	B, C	1, 2

*TGA conditions are given in each TGA profile.

From these final tests, it can be concluded that the TGA method lacks the selectivity required for use as a criterion for silane primer batch evaluation.

3. HPLC and GC Analysis of DC 1200 Silane Primers

HPLC Method:

A series of DC 1200 silane primers were analyzed by HPLC using Sep Pak (silica 10 µ, 10 cm x 4.6 mm i.d.) cartridges with hexane chloroform (1:1) as mobile phase and refractive index detector. As the profiles in Fig. 8 (isopropanol* and proponal standards) and Fig. 9 (DC 1200 primer samples) indicate, no conclusive pattern could be found correlating the FTIR increase in OH-absorption and an increase in the first HPLC peak of each silane sample.

GC Method:

Although previous GC studies had not proved conclusive, it was believed that there should be a GC method which could quickly determine the alcohol content of different DC 1200 silane batches. Analyses with a new GC method have been initiated, where only the headspace of the individual primer samples will be analyzed for alcohols. Initial correlations between samples with higher IR absorbance in the OH- region and alcohols content (by GC) seems to be good enough that all previously analyzed silanes will be examined by this method and reported in the 11th report.

Preliminary results for samples 6, 7 and C are given in the tables below. Their chromatographic profiles are shown in Figs. 10 to 13. It can be seen that the most degraded sample C (Fig. 11) contains the largest quantity of hydrolyzed products (some of which have to be further determined by GC/MS).* A GC profile of sample #6 in Fig. 12 indicates only a moderate release of an "alcoholic fraction" due to hydrolysis. The newest sample #7, recently received from NASA shows only a minimal presence of OH bonds by FTIR. This finding correlates with the GC profile of the polar fraction, where almost no decomposition products have been detected (Fig. 13). Fig. 10 gives a GC profile of a blank.

A preliminary calculation of total isopropanol and n-butanol content** are indicated in the following table:

% Isopropanol + n-butanol	Sample ID #
3.2%	6
3.6%	7
9.9%	C

*To be included in 11th report.

**Detection based on retention times of standards only.

If some unidentified GC peaks are considered to be silane hydrolytic products, the percent decomposition in the silanes might be:

5.0% in sample #7

11.7% in sample #6

25.2% in sample #C

The GC conditions used were as follows: GC glass column (6' x 2mm i.d.) filled with 5% Carbowax 20M on Carbopack B, 100/120 mesh; temperature program started at 70°C, heated at 5°/min. to 170°C; helium as a carrier gas, flow rate 27 ml/min. Only 5-10 µl of headspace was used for GC analysis. Further analyses are in progress.

4. Determination of Titanium and Silicon By Atomic Absorption Spectrometry (Method Description)

Six DC 1200 silane coupling agents received from NASA (our ID # 1-6) and two samples previously obtained (B and C) were first analyzed for their residue content. Ten ml of each sample was pipetted (in duplicate) into platinum crucibles, placed in an air-forced oven for 3 hours at 105°C, and then weighed for residue content. The platinum crucibles with residues were then placed in a muffle furnace overnight at 600°C. After cooling in a desiccator, the samples were weighed for ash content.

To each sample ash was added approximately 20X by weight of $LiBO_2$. The powders were well mixed and then placed in a muffle furnace at 900°C for 15-30 minutes. Mixtures were swirled several times to insure complete fluxing. After removing the Pt crucibles from the muffle furnace, they were quenched in a beaker of cold water. The flux material was then dissolved in the presence of distilled water and HNO_3 (with heating), 5 drops of HF (HF was added into the cooled solution to prevent loss of Si as SiF_6) and 20 drops of H_2O_2. The contents were then transferred to a 1000 ml volumetric flask. A completely clear yellow solution resulted. (The HNO_3 concentration of the final solutions were approximately 5% HNO_3).

A blank with the same concentration of reagents was also prepared.

Instrumental analyses were conducted with an atomic absorption spectrometer (Model 450, Perkin Elmer). Silicon was measured at 251.7 nm; 0.2 nm slit width; N_2O/acetylene flame (linearity to 150 ppm). Titanium was measured at 365.6 nm, 0.2 nm slit width, N_2O/acetylene flame (linearity to 200 ppm).

A protocol with the results obtained for Si and Ti contents in six DC 1200 silane samples is enclosed in the Appendix (pgs. A-1 to A-5).

The table on page 6 summarizes the DC 1200 primer results for:

1) residue content
2) ash analysis
3) analyses of titanium, silicon and their ratio (Si/Ti)
4) OH- absorptions (3360-3470 cm^{-1})
5) average PSI values from preliminary lap sheer tests (see more in the next report #10)

5. Plan For Future Work

On January 6, 1985 the continuation work outlined in the Amendment No. 1 was initiated. A progress report covering the period 1/6/85 - 3/20/85 will be issued as the 10th report.

As agreed with the project monitor, Mr. Don Morris, the final report will be issued after concluding this amended work (concluding date June 1, 1985).

6. Financial Status

The total cumulative expenditure incurred as of the report date, December 1, 1985, is $45,627 (i.e., material and labor). The estimated percentage of contract completion (excluding Amendment No. 1) is 100%.

Summary of Results Obtained for DC 1200 Silane Primers

(Residue, Ash, Titanium, Silicone, Si/Ti Ratio,
OH-Absorption, Lap Sheer Test,
GC Headspace for Alcohols)

DC Primer Lot #	% Residue Content @ 105°C	% Ash (800°C)		Titanium %		Silicone %		Ratio Si/Ti	Abs. Units = Abs. height (mm) x Abs. unit/inch / 25 mm/inch				Lap Sheer Test Avg. psi**	Preliminary GC Analysis of Alcohols***
		Dupl.	Avg.	Dupl.	Avg.	Dupl.	Avg.		3360 cm^{-1}	3300 cm^{-1}	3420 cm^{-1}	3470 cm^{-1}		
A	4.86	2.86 2.77	2.82	0.579 0.642	0.61	0.601 0.705	0.65	1.07						
B	5.07	2.75 2.69	2.72	0.604 0.558	0.58	0.747 0.815	0.78	1.34	1.2204	1.1232	0.972	0.776	79.55 (9 pts)	-
C	4.15	3.00 3.10	3.05	0.509 0.567	0.54	0.633 0.688	0.66	1.22	1.7716	1.6168	1.7200	1.3244	51.33 (9 pts)	25.2
1	3.51	2.96 3.07	3.02	0.66 0.64	0.65	0.88 0.91	0.90	1.38	0.4620	0.4620	0.4620	0.4788	*	-
2	3.84	3.14 3.07	3.10	0.62 0.61	0.62	0.89 0.87	0.88	1.42	0.7176	0.6992	0.6532	0.5796	91.0 (9 pts.)	-
3	3.70	3.17 3.09	3.14	0.62 0.62	0.62	0.95 0.91	0.93	1.50	1.1252	1.0440	0.9744	0.7772	84.66 (3 pts)	-
4	3.35	3.14 3.17	3.16	0.61 0.60	0.61	0.96 0.96	0.96	1.57	0.6636	0.6636	0.6636	0.5628	*	-
5	3.56	3.36 3.14	3.4	0.62 0.65	0.64	1.00 1.02	1.01	1.58	0.5688	0.5544	0.5472	0.5328	152.0 (5 pts)	-
6	3.78	3.15 3.17	3.16	0.62 0.61	0.62	0.93 0.93	0.93	1.50	0.3016	0.3068	0.3276	0.3484	*	11.7
7	4.48	3.03 3.02	3.03	*		*		*	0.0288	0.0144	0.0048	0.0144	177.33 (6 pts)	5%

*Results will be included in report #11.
**Preliminary results, see in detail report #10.
***Total of alcohols found in headspace.

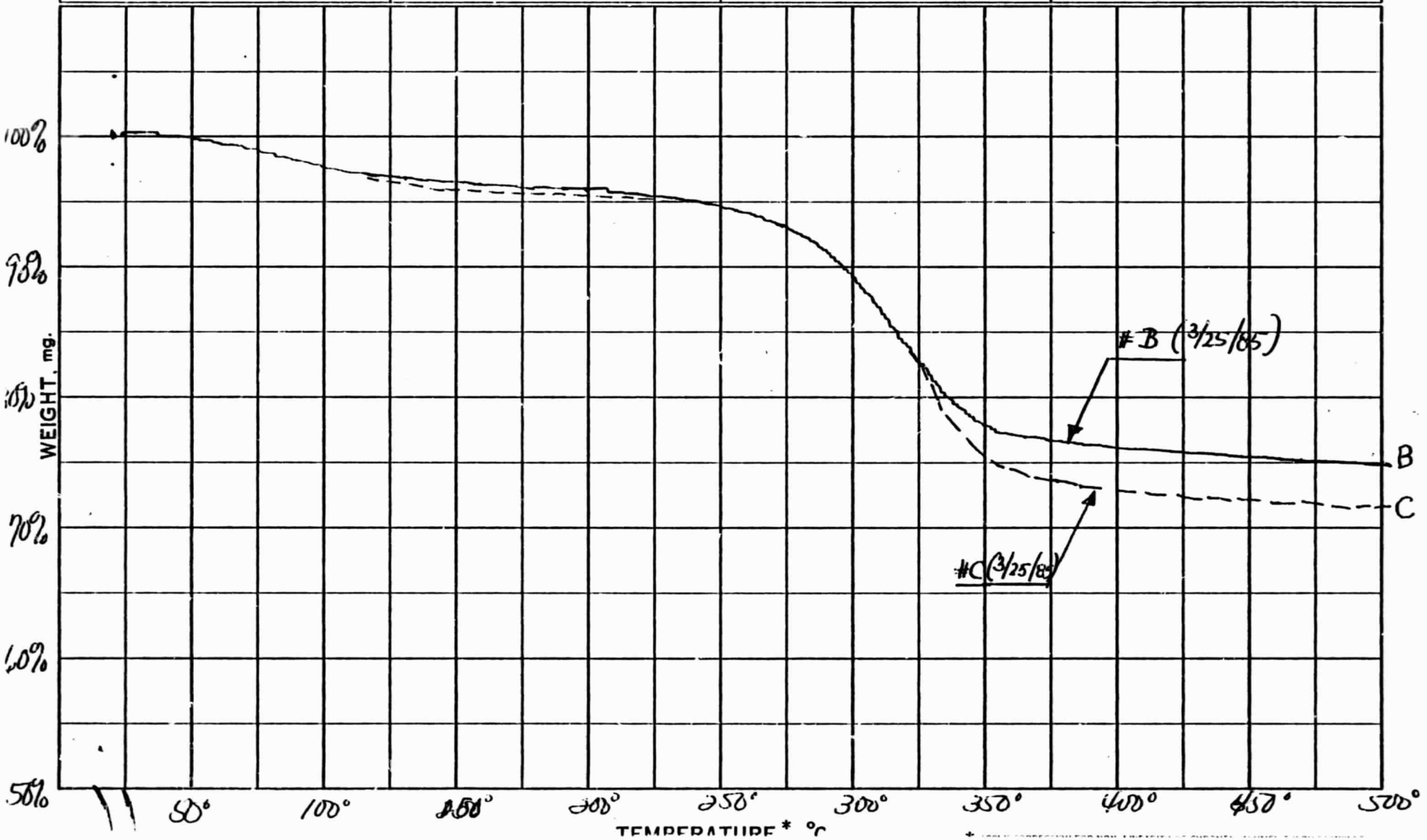
PART NO. 950611

Nasa 6031.2

DUPONT INSTRUMENTS

FIG. 1

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. 2180 DATE 3-25-85
Sample B	TEMP. SCALE 50 °C/inch	SCALE ____ mg./inch	OPERATOR C. A. Mowrey
SIZE 21.8 mg.	SHIFT ____ inch	(SCALE SETTING X 2)	HEATING RATE 20 °C/min.
	TIME SCALE (ALT.) ____	SUPPRESSION 10.8 mg.	ATM. N_2
			TIME CONSTANT 2 sec.



Nasa 6031.2

DUPONT INSTRUMENTS

FIG. 2

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. 2181 DATE 3-25-85
Sample C	TEMP. SCALE 50 °C/inch	SCALE ____ mg./inch	OPERATOR C. A. Mowery
SIZE 22.6 mg.	SHIFT ____ inch	(SCALE SETTING X 2)	HEATING RATE 20 °C/min.
	TIME SCALE (ALT.) ____	SUPPRESSION 12.6 mg.	ATM. N_2
			TIME CONSTANT 2 sec.

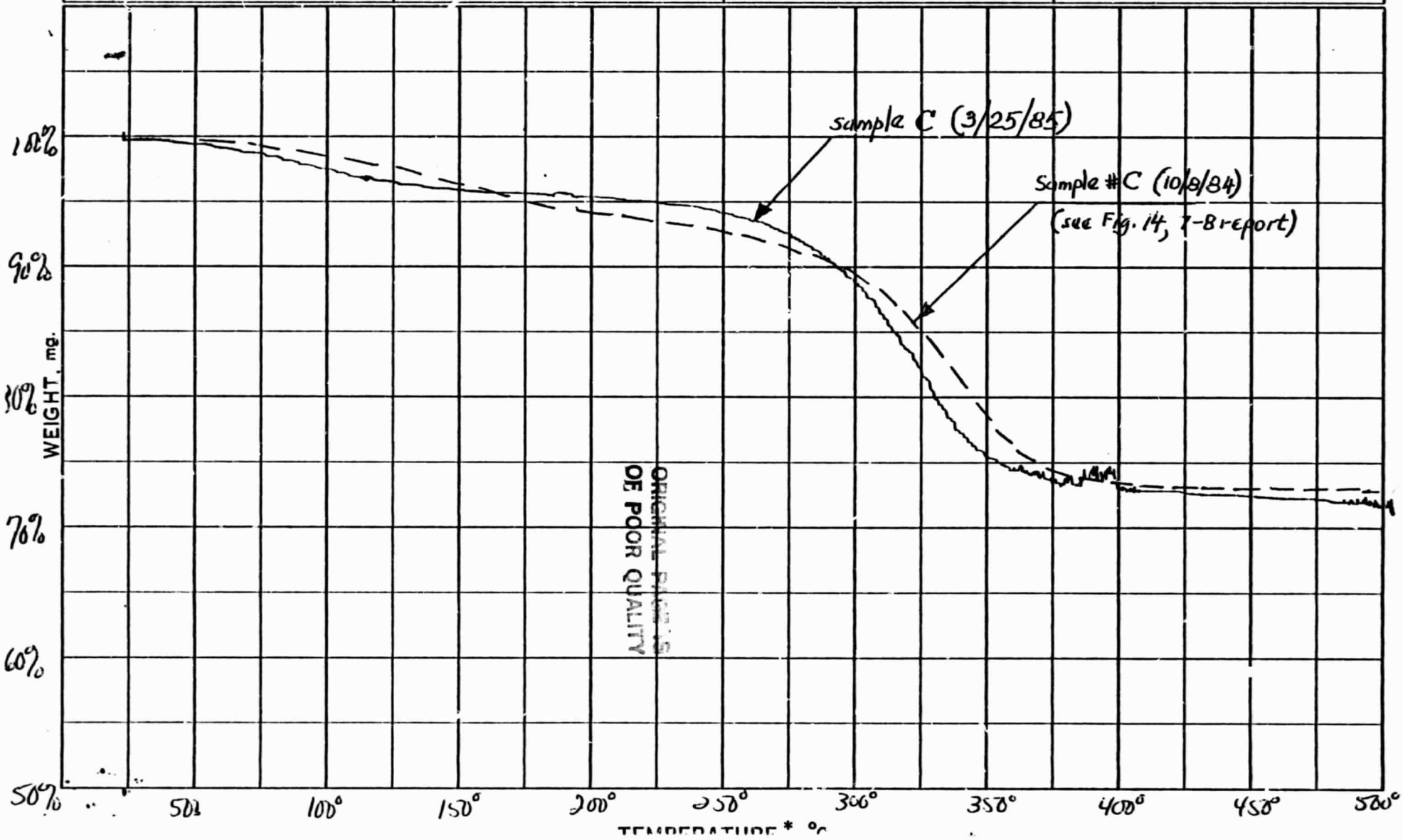
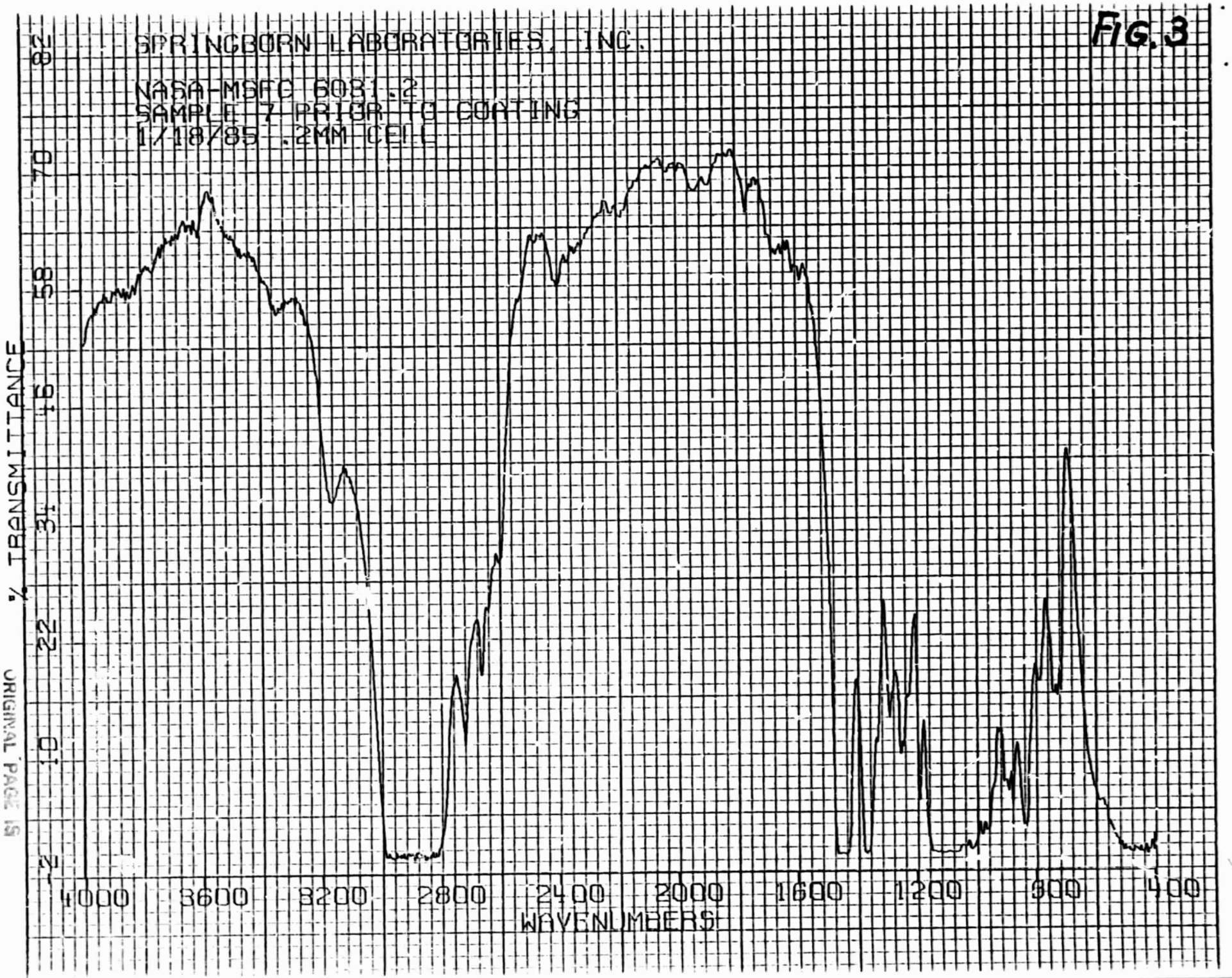


FIG. 3



PART NO. 950611

Nasa 6031.2

DUPONT INSTRUMENTS

FIG. 4

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. 2182 DATE 3-26-85
Sample 7	TEMP. SCALE 50 °C/inch	SCALE 4 mg./inch	OPERATOR C.A. Mowery
SIZE 20.2 mg.	SHIFT ____ inch	(SCALE SETTING X 2)	HEATING RATE 20 °C/min.
	TIME SCALE (ALT.) ____	SUPPRESSION 10.2 mg.	ATM. N_2
			TIME CONSTANT 2 sec.

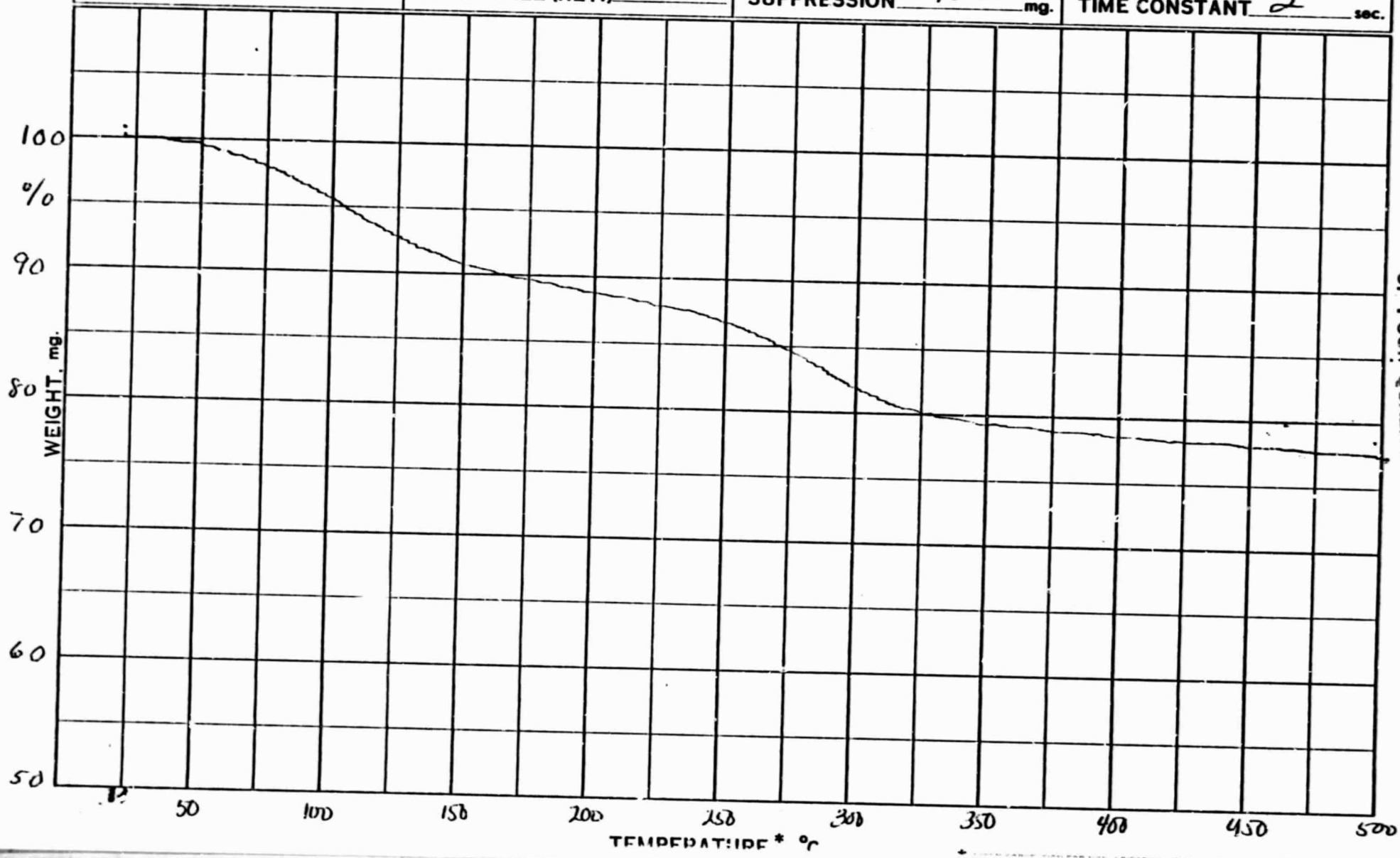


FIG. 5

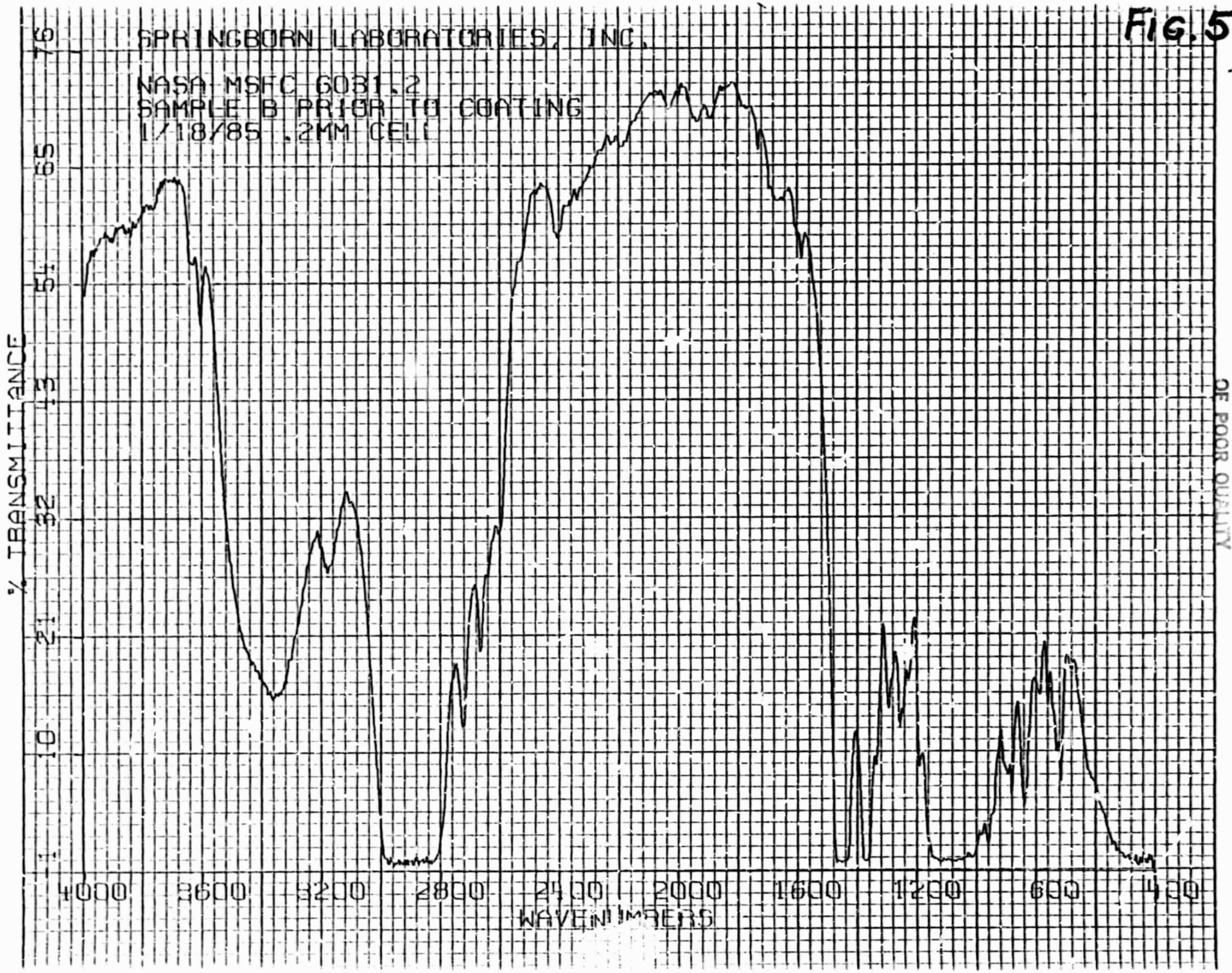
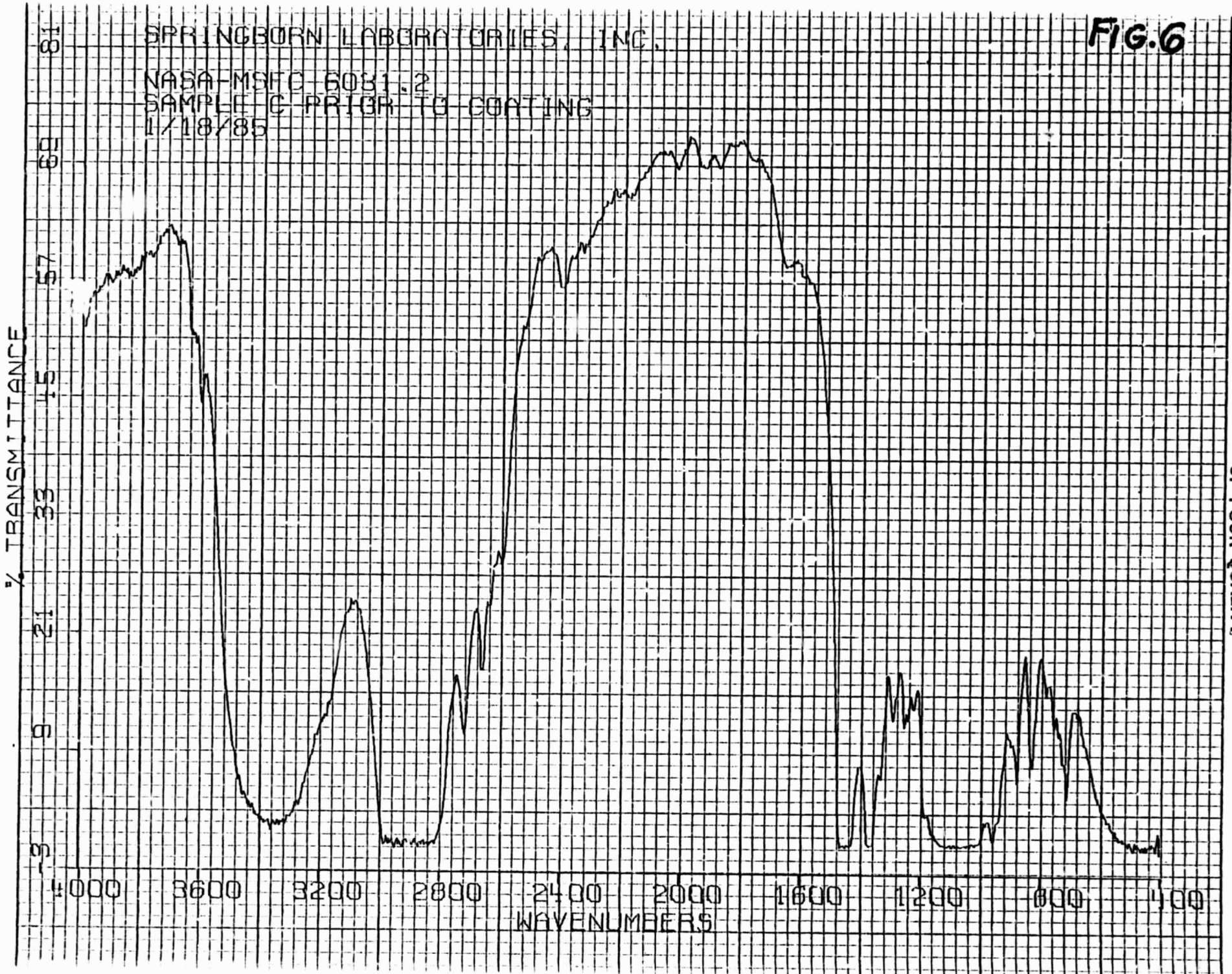


FIG.6



DUPONT INSTRUMENTS

FIG. 7

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
SIZE ____ mg.	TEMP. SCALE ____ °C/inch	SCALE ____ mg./inch	OPERATOR ____
	SHIFT ____ inch	(SCALE SETTING X 2)	HEATING RATE ____ °C/min.
	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	ATM. ____
			TIME CONSTANT ____ sec.

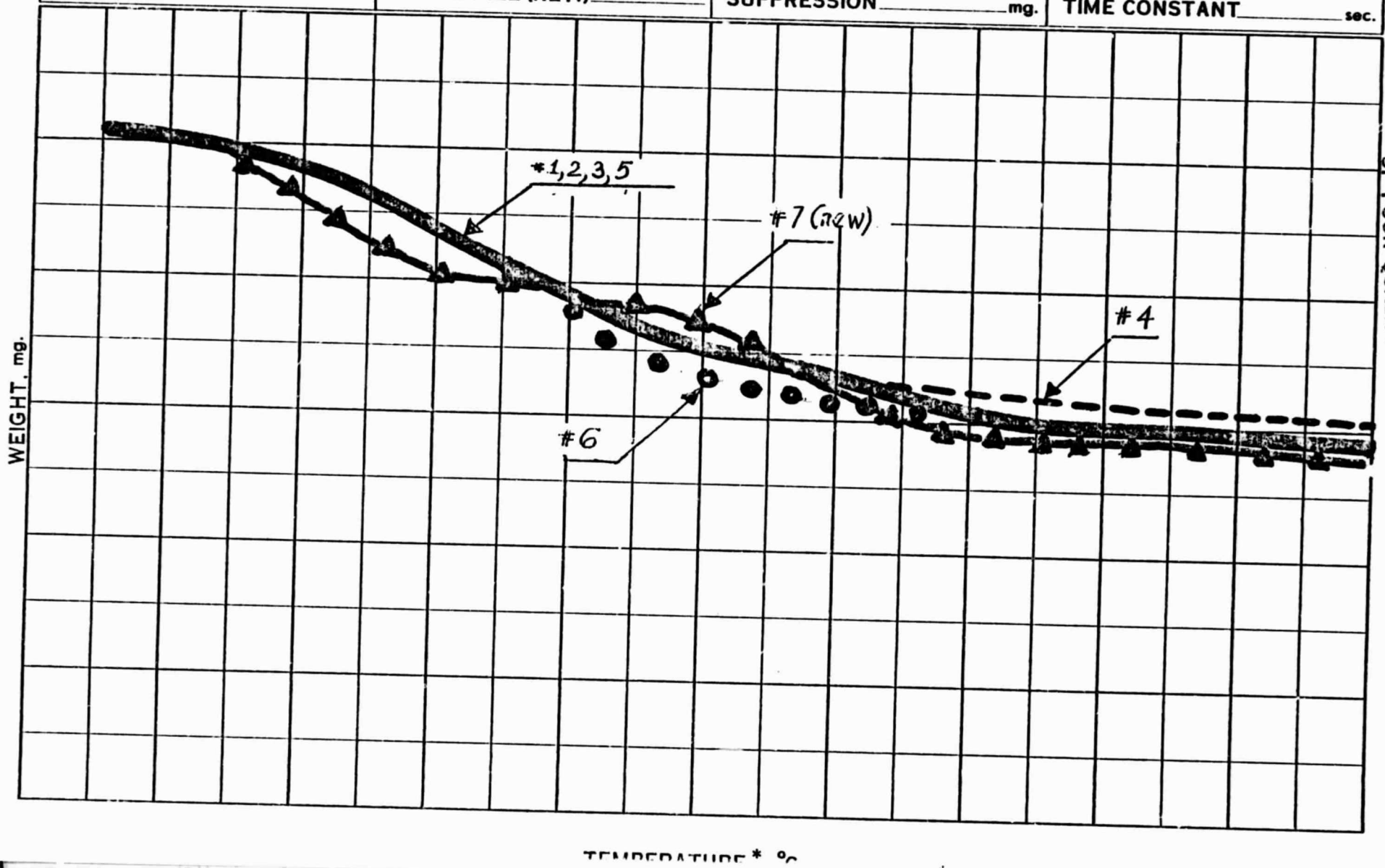
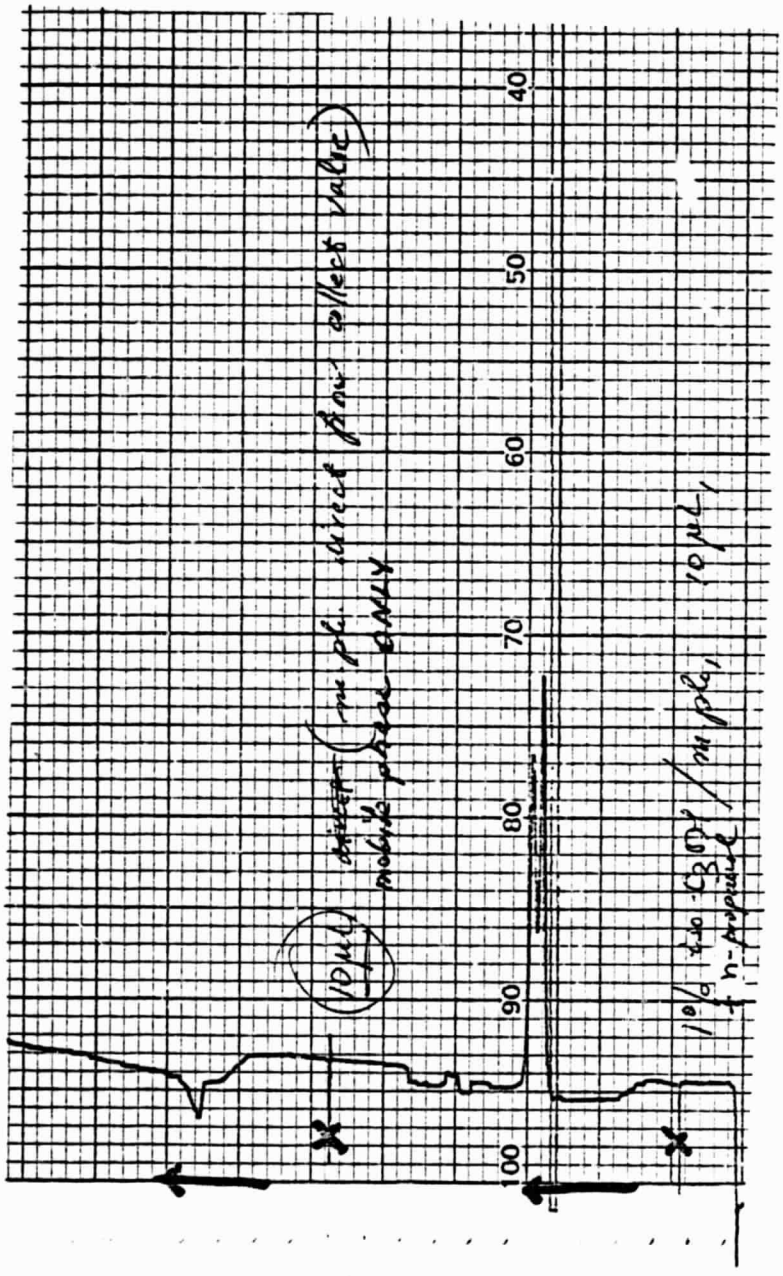


FIG. 8



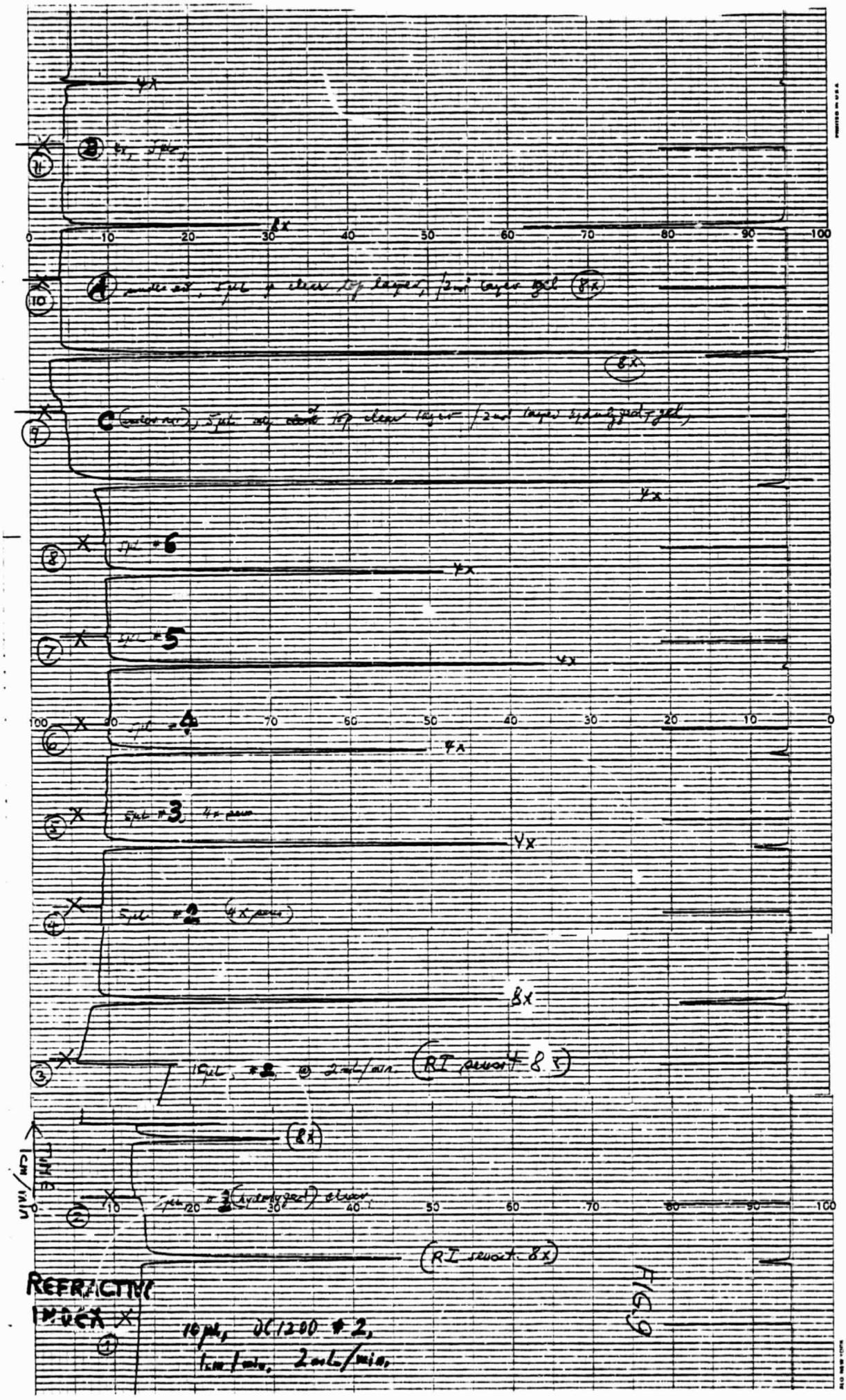
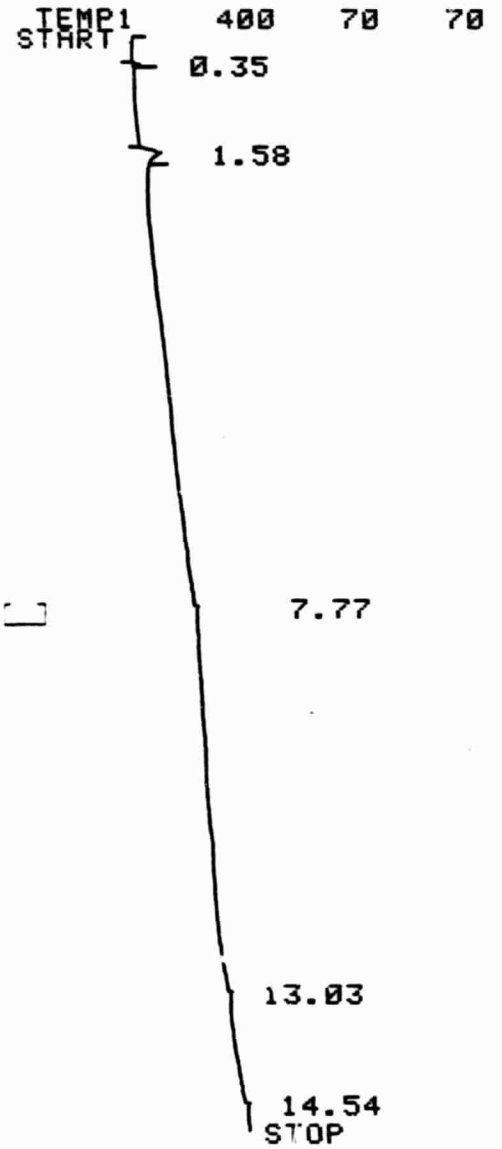


Fig 9

FIG. 10

GC of blank



HP RUN # 152 APR/05/85 TIME 15:31:18
AREA %

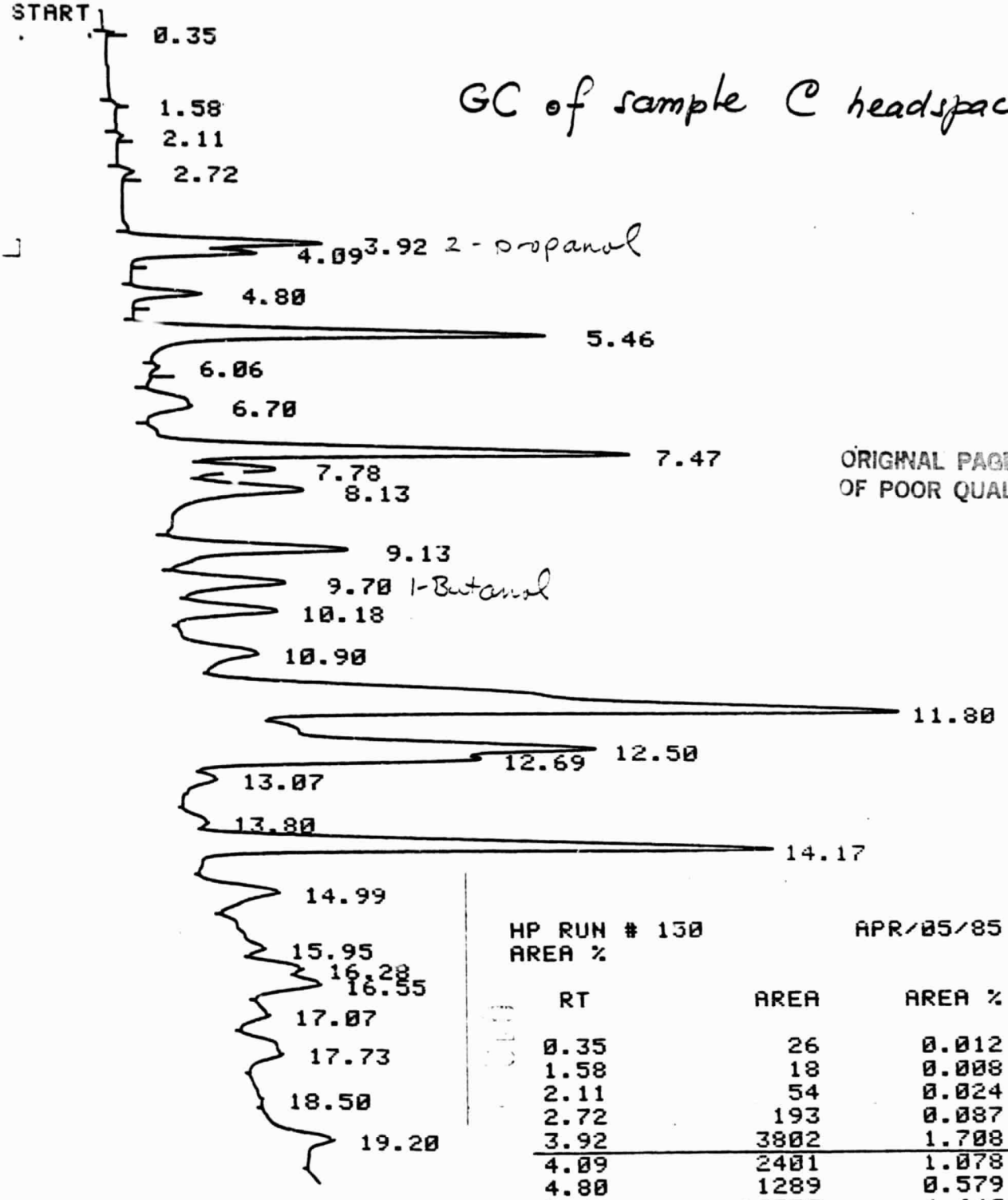
RT	AREA	AREA %
0.35	11	5.556
1.58	187	94.444

DIL FACTOR: 1.0000 E+ 0

TEMP1 400 70 70

FIG. 11

GC of sample C headspace



TIME 14:33:46

HP RUN # 130 APR/05/85
AREA %

RT	AREA	AREA %	
0.35	26	0.012	
1.58	18	0.008	
2.11	54	0.024	
2.72	193	0.087	
3.92	3802	1.708	2-propanol
4.09	2401	1.078	
4.80	1289	0.579	
5.46	10330	4.640	
6.06	240	0.108	
6.70	1890	0.849	
7.47	13230	5.942	
7.78	3639	1.634	
8.13	8282	3.720	
9.13	7214	3.240	
9.70	5424	2.436	1-butanol
10.18	5173	2.323	
10.90	7856	3.528	
11.80	40350	18.123	
12.50	21180	9.513	
12.69	9140	4.105	
13.07	3854	1.731	
13.80	3659	1.643	
14.17	22830	10.254	

ESCAPE

FIG. 12

GC of sample #6 headspace

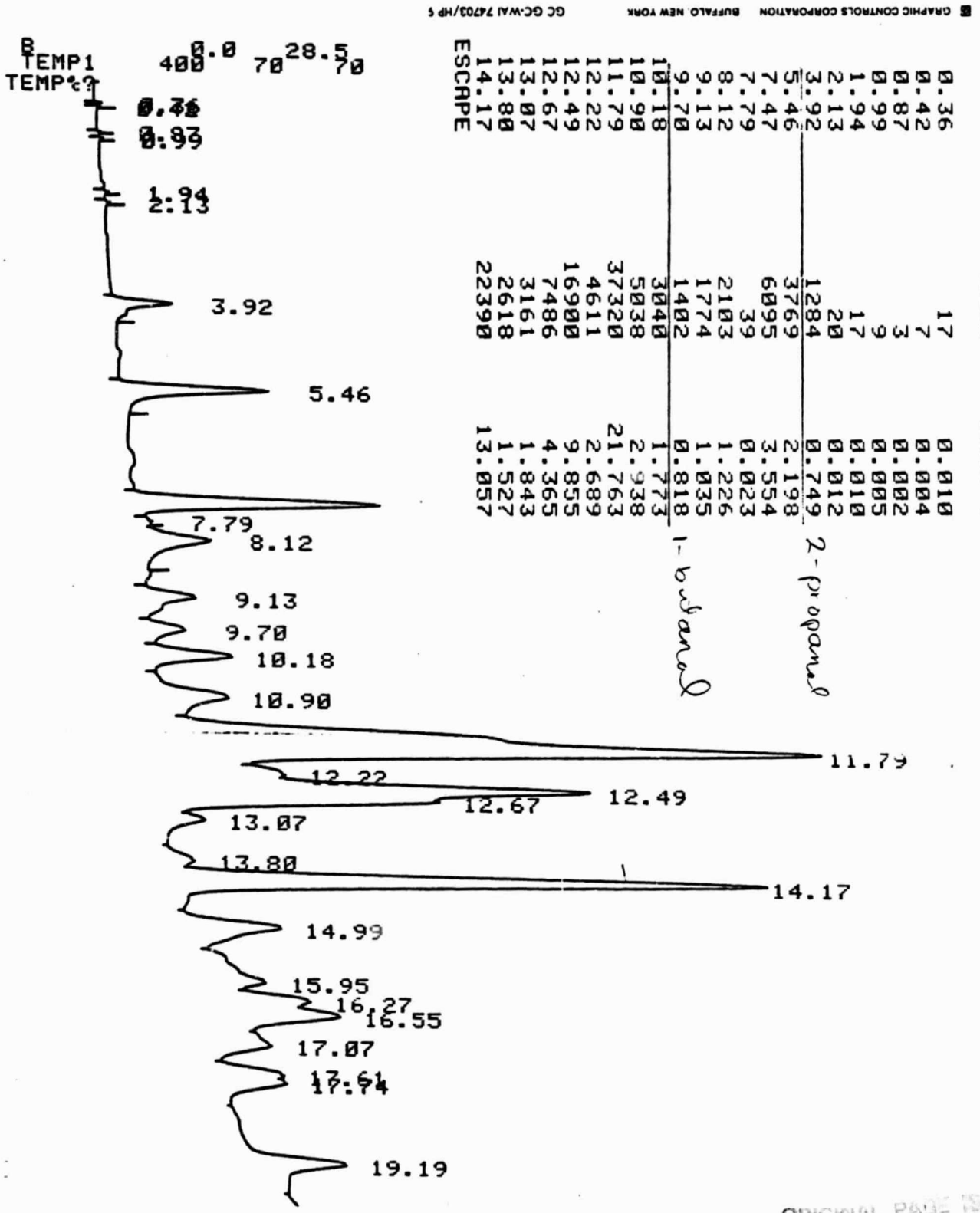
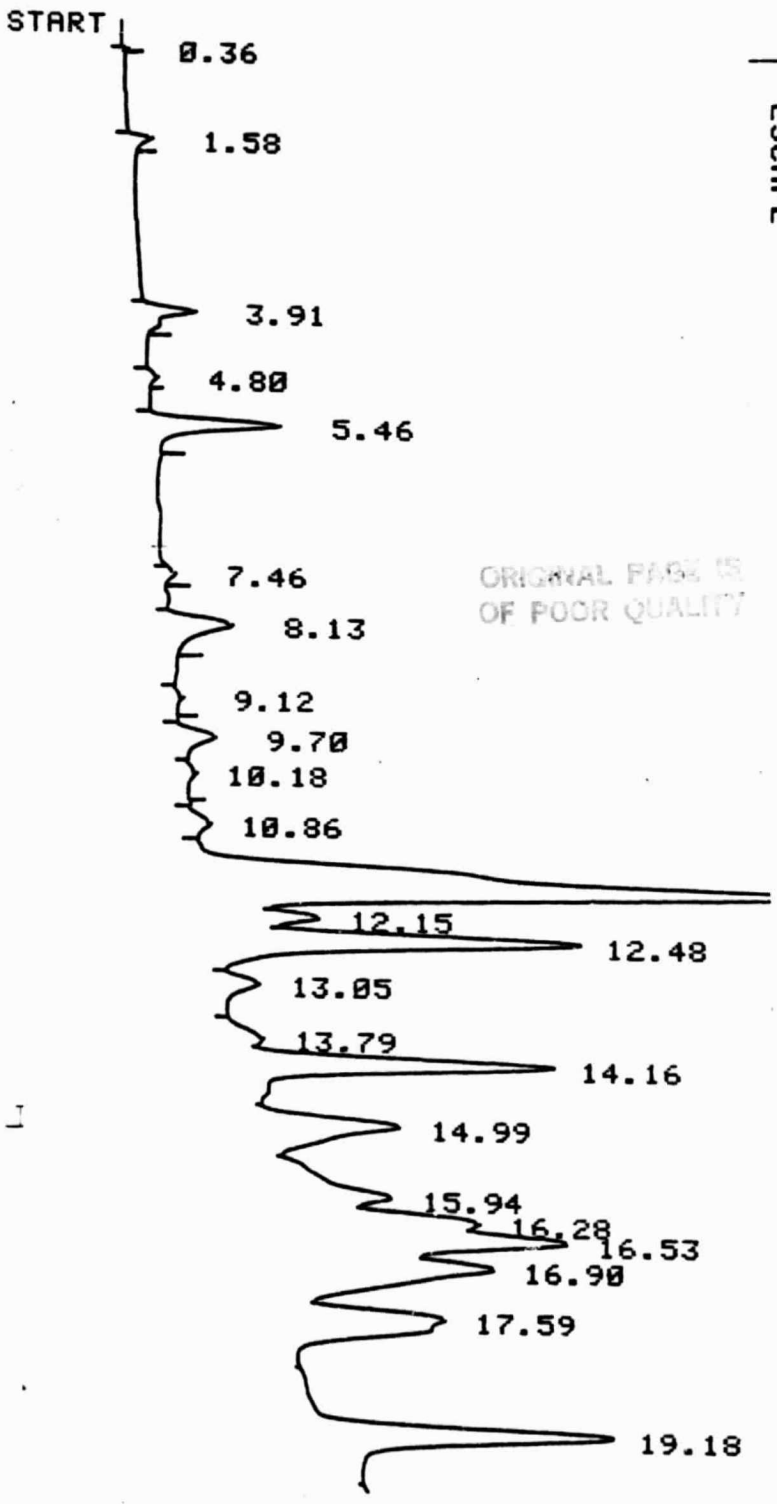


FIG. 13

GC of sample #7 headspace



ROLS CORPORATION BUFFALO, NEW YORK GC GC:WAI 7673/HP 9270-0625

HP RUN # 153 APR/05/85 TIME 15:53:32
AREA %

	RT	AREA	AREA %
	0.36	12	0.009
	1.58	230	0.163
	3.91	954	0.677
	4.80	103	0.073
	5.46	2403	1.706
	7.46	145	0.103
	8.13	1634	1.160
	9.12	103	0.073
	9.70	878	0.623
	10.18	230	0.163
	10.86	507	0.360
	11.78	25160	17.860
	12.15	3186	2.262
	12.48	11820	8.390
	13.05	2802	1.989
	13.79	3686	2.616
	14.16	13510	9.590
	ESCAPE		

APPENDIX

PROTOCOL:	Atomic Absorption Spectrometry
SAMPLE(s)	Six DC 1200 Silane Primers
ANALYZED FOR:	Si and Ti
ANALYST:	Connie C. Cantor

36408

NASA 6031.2

6/7/84

Instrumental Analysis

Silicon 251.7nm — N_2O/C_2H_2 flame
0.2 mm slit width — linear to 150ppm

Standards	ABSORBANCE						AVG ABS	ABS/ppm
10ppm	0.021	0.020	0.019	0.021	0.022	0.021	0.0208	0.00208
25ppm	0.040	0.041	0.041	0.042	0.040	0.042	0.0411	0.00164
50ppm	0.075	0.077	0.076	0.075	0.076	0.075	0.0756	0.00151
75ppm	0.114	0.112	0.115	0.113	0.114	0.113	0.1135	0.00151

AVG ABS/ppm = 0.0015

Samples							
Blank	-0.001	0.000	-0.000	0.001	-0.002	0.001	0.000
3-2	0.112	0.110	0.111	0.107	0.112	0.112	0.111
4-2	0.111	0.110	0.112	0.110	0.112	0.109	0.111
5-2	0.116	0.117	0.118	0.116	0.115	0.117	0.116
6-2	0.119	0.121	0.118	0.120	0.121	0.119	0.119
8-2	0.108	0.107	0.109	0.108	0.109	0.109	0.108
9-2	0.107	0.108	0.109	0.110	0.109	0.107	0.108
3-3	0.101	0.100	0.099	0.101	0.100	0.102	0.101
4-3	0.102	0.105	0.104	0.105	0.106	0.103	0.104
5-3	0.102	0.103	0.101	0.103	0.104	0.102	0.103
6-3	0.099	0.101	0.102	0.103	0.100	0.103	0.101
8-3	0.110	0.111	0.110	0.109	0.111	0.112	0.110
9-3	0.107	0.105	0.106	0.107	0.105	0.106	0.106

Calculations

3-3 #1: $\frac{0.101 \text{ ABS}}{0.0015 \frac{\text{ABS}}{\text{ppm}}} = 67.33 \text{ ppm} \times 1000 \text{ ml} = \frac{67333 \text{ ug}}{7.63 \text{ gm}} = 8825 \frac{\text{ug}}{\text{gm}}$

4-3 #1: $\frac{0.104}{0.0015} = 69.33 \times 1000 = \frac{69333}{7.63} = 9087 \frac{\text{ug}}{\text{gm}}$

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TI 36409

PROJECT TITLE NASA

PROJECT NO 6031-2

DATE 6/7/84

5-3 #2 $\frac{0.103}{0.0015} = 68.66 \times 1000 = \frac{68666}{7.73 gm} = 8883 \mu g/gm$

6-3 #2 $\frac{0.101}{0.0015} = 67.33 \times 1000 = \frac{67333}{7.73 gm} = 8710.$

8-3 #3 $\frac{0.110}{0.0015} = 73.33 \times 1000 = \frac{73333}{7.73 gm} = 9487$

9-3 #3 $\frac{0.106}{0.0015} = 70.66 \times 1000 = \frac{70666}{7.73 gm} = 9142$

3-2 #4 $\frac{0.111}{0.0015} = 74.0 \times 1000 = \frac{74000}{7.73} = 9573$

4-2 #4 $\frac{0.111}{0.0015} = 74.0 \times 1000 = \frac{74000}{7.73} = 9573$

5-2 #5 $\frac{0.116}{0.0015} = 77.33 \times 1060 = \frac{77333}{7.73} = 10004$

6-2 #5 $\frac{0.079}{0.0015} = 79.33 \times 1000 = \frac{79333}{7.73} = 10263$

8-2 #6 $\frac{0.108}{0.0015} = 72.0 \times 1000 = \frac{72000}{7.73} = 9314$

9-2 #6 $\frac{0.108}{0.0015} = 72.0 \times 1000 = \frac{72000}{7.73} = 9314$

S_ TESTING INSTITUTE
SOUTHEASTERN LABORATORIES, INC.

TI 36410

PROJECT NAME NASA PROJECT NO 60312

DATE 6

Ti 365.6nm
0.2nm slit width

N_2O/C_2H_2 flame
linear to 200ppm

Standards							AVG Abs	Abs/ppm
10 ppm	0.039	0.038	0.039	0.039	0.037	0.040	0.0384	0.00384
25 ppm	0.076	0.075	0.074	0.075	0.076	0.075	0.075	0.0030
50 ppm	0.129	0.132	0.132	0.130	0.129	0.128	0.130	0.0026
100 ppm	0.234	0.235	0.235	0.238	0.235	0.238	0.236	0.0024
Samples							AVG Abs/ppm	0.0027
Blank	-0.001	0.001	-0.002	0.001	0.000	0.001	0.000	
3-3	0.136	0.135	0.136	0.138	0.137	0.135	0.136	
4-3	0.128	0.132	0.130	0.132	0.134	0.136	0.132	
5-3	0.129	0.129	0.132	0.130	0.129	0.128	0.130	
6-3	0.128	0.129	0.127	0.129	0.128	0.129	0.128	
8-3	0.133	0.126	0.132	0.127	0.133	0.129	0.130	
9-3	0.136	0.131	0.129	0.131	0.128	0.127	0.129	
3-2	0.125	0.127	0.128	0.126	0.129	0.125	0.127	
4-2	0.126	0.127	0.125	0.126	0.127	0.123	0.126	
5-2	0.128	0.132	0.129	0.129	0.128	0.127	0.129	
6-2	0.135	0.136	0.135	0.134	0.136	0.133	0.135	
8-2	0.130	0.129	0.131	0.130	0.129	0.129	0.130	
9-2	0.129	0.129	0.128	0.129	0.127	0.126	0.128	

Calculations

3-3 #1 $\frac{0.136}{0.0027} = 50.37 \times 1000 = \frac{50370}{7.63} = 6602$ µg/gm

4-3 #1 $\frac{0.132}{0.0027} = 48.88 \times 1000 = \frac{48886}{7.63} = 6407$ µg/gm

5-3 #2 $\frac{0.130}{0.0027} = 48.15 \times 1000 = \frac{48148}{7.73} = 6229$ µg/gm

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6-3 #2 $\frac{0.128}{0.0027} = 47.4 \times 1000 = \frac{47407}{7.73} = 6133.$

8-3 #3 $\frac{0.130}{0.0027} = 48.14 \times 1000 = \frac{48148}{7.73} = 6229$

9-3 #3 $\frac{0.129}{0.0027} = 47.77 \times 1000 = \frac{47777}{7.73} = 6181$

3-2 #4 $\frac{0.127}{0.0027} = 47.04 \times 1000 = \frac{47037}{7.73} = 6085$

4-2 #4 $\frac{0.126}{0.0027} = 46.66 \times 1000 = \frac{46666}{7.73} = 6037$

5-2 #5 $\frac{0.129}{0.0027} = 47.77 \times 1000 = \frac{47777}{7.73} = 6181$

6-2 #5 $\frac{0.135}{0.0027} = 50.0 \times 1000 = \frac{50000}{7.73} = 6468$

8-2 #6 $\frac{0.130}{0.0027} = 48.14 \times 1000 = \frac{48148}{7.73} = 6229$

9-2 #6 $\frac{0.128}{0.0027} = 47.407 \times 1000 = \frac{47407}{7.73} = 6133$

Residues at 105°C - 5 mls each sample

sample	wt al pan	wt w/ residue (1 hr)	wt w/ residue (2 hrs)	overnight wt w/ residue	% residue
1	1.4338	1.5810	1.5759	1.5677	3.51
2	1.4369	1.6004	1.5951	1.5855	3.84
3	1.3751	1.5331	1.5258	1.5180	3.70
4	1.4351	1.5745	1.5701	1.5649	3.35
5	1.3829	1.5358	1.5290	1.5204	3.56
6	1.4264	1.5702			

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Summary

	Residue @ 105°C	% Ash Dupl	% Ash Avg	% Ti	% Ti Avg	% Si	% Si Avg	Ratio Si/Ti
1	3.51	~~3.41~~ 2.9 ~~3.57~~ 3.0	3.02	0.66 0.64	0.65	0.88 0.91	0.90	1.38
2	3.84	~~3.34~~ 3.07	3.10	0.62 0.61	0.62	0.89 0.87	0.88	1.42
3	3.70	3.19 3.09	3.14	0.62 0.62	0.62	0.95 0.91	0.93	1.50
4	3.35	3.14 3.17	3.16	0.61 0.60	0.61	0.96 0.96	0.96	1.57
5	3.56	3.36 3.44	3.40	0.66 0.65	0.64	1.00 1.02	1.01	1.58
6	3.78	3.15 3.17	3.16	0.62 0.61	0.62	0.93 0.93	0.93	1.50